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Observation of a metastable defect transition in GaAs

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We show that the well-known 0.15-eV donor in bulk GaAs quenches under IR-light illumination and that the quenched (metastable) state has an electronic transition energy about 0.14 eV deeper than the ground state and can be observed by temperature-dependent-resistivity and Hall-effect measurements. The quenched state thermally recovers by an Auger-like process at a rate of $r=2.3\times10^{-12}$ $nv_n\exp(-0.18/kT)$. Many of the properties exhibited by this donor are similar to those predicted theoretically for the complex defect As_{Ga}-V_{As}.

As impurity concentrations have been reduced, defects have assumed a more dominant role in GaAs, one of the most important semiconductor materials. Of all the possible defects, however, only two have been identified with any degree of certainty: the As vacancy (V_{As}) in electron-irradiated GaAs, and the As antisite (As_{Ga}) in bulk, neutron-irradiated, and plastically deformed GaAs. By far the most studied defect in GaAs is *EL*2, known to be related to As_{Ga} and having a deep donor level at $E_C-0.75$ eV ($T=0$ value).[1–3] One reason for the great amount of fundamental interest in *EL*2 is the existence of a metastable state ($EL2^*$), evidently formed by a displacement of the As atom in a $\langle 111 \rangle$ direction.[4,5] A donor transition associated with this state has not been directly observed by optical or electrical experiments, presumably because the two available donor electrons are in a deep state very close to the valence band.[4,5] An acceptor state of $EL2^*$ has been recently observed, but only under pressure.[6,7]

Besides that of *EL*2, the only other transitions commonly observed in the upper half of the GaAs band gap are the shallow (hydrogenic) impurity levels, and deep levels located at $E_C-0.15$ eV and $E_C-0.43$ eV.[8,9] Neither of these latter centers has been positively identified, although both have been shown to be pure defects.[10,11] It has been suggested that the $E_C-0.15$-eV defect in bulk GaAs is related to the As vacancy, because that defect has been identified in 1-MeV electron-irradiated GaAs, and indeed has a donor level at about $E_C-0.15$ eV. However, the bulk and irradiation defects could not be identical because the latter are unstable and anneal out above 300 °C.[12] In this work, we show that the bulk and irradiation 0.15-eV centers are definitely different by comparing their quenching properties; the irradiation defect does not quench while the bulk defect strongly quenches. The latter has some properties very similar to those of the As_{Ga}-V_{As} defect, theoretically analyzed in detail by Baraff and Schluter.[13] Whatever the identity of the defect, we are able to observe the electronic properties of its metastable state by using the methodology described in this paper.

The $E_C-0.15$-eV center has been observed by resistivity and Hall-effect measurements many times over the last two decades, both in horizontal Bridgman (HB) and liquid-encapsulated Czochralski (LEC) crystals.[8–10,14] A sample in this energy range is quite amenable to analysis by temperature-dependent Hall (TDH) measurements, and the concentration of the center can accurately be determined. Typically, in cases for which the Fermi level E_F is controlled by the 0.15-eV defect, we have found its concentration N_D to be in the mid-10^{15}- to low-10^{16}-cm^{-3}, range, usually much higher than impurity concentrations, including oxygen, and also higher than the *EL*2 concentration.[10] Parameters such as N_D are found by fitting the TDH data to the charge-balance equation, written here for the case of two donors:[15]

$$n+N_A^{\rm net}=\frac{N_{D1}}{1+n/\phi_1}+\frac{N_{D2}}{1+n/\phi_2}, \qquad (1)$$

where $N_A^{\rm net}=N_{AS}-N_{DS}$, and $N_{DS}(N_{AS})$ is the concentration of all donors (acceptors) lying well above (below) E_F, and

$$\phi_i=\frac{g_{ui}}{g_{oi}}N_C' e^{\alpha_i/k}T^{3/2}e^{-E_{Di}/kT}, \qquad (2)$$

where $g_u(g_o)$ is the degeneracy of the unoccupied (occupied) donor state, N_C' is the conduction-band density of states at $T=1$ K, E_D is the donor activation energy (0.15 eV, in this case), and α is a temperature coefficient defined by $E_D=E_{D0}-\alpha T$. By fitting the one-donor model ($N_{D2}=0$) to sample CS 3417 from $T=140$–420 K (cf. Fig. 1 of Ref. 10), we find that $N_D=9\times10^{15}$, $N_A^{\rm net}=4\times10^{15}$ cm^{-3}, $E_{D0}=0.153$ eV, and $(g_u/g_o)\exp(\alpha/k)\simeq1.5$. Other samples exhibit similar parameters. For maximum accuracy in the n vs T fits, the Hall r factors ($n=r/eR$) were calculated by an iterative solution of the Boltzmann equation; however, their values varied only between 1.02 and 1.18 in the given temperature range, and were inconsequential.

For the quenching experiments, it was much more convenient to measure current I vs T, rather than n vs T, be-

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cause of the speed of gathering data. A commercial deep-level transient spectroscopy (DLTS) system (BioRad DL4600) was used for the temperature control, and an electrometer was used to measure current. An IR-light source was provided by a 25-W white light covered by a Si filter, so that $h\nu \leq 1.12$ eV. The maximum IR-light intensity was about 10^{16} photons/cm^2 s.

Quenching data are presented in Fig. 1. In this experiment, the sample was cooled to 82 K in the dark, then the IR light was turned on for about 5 min. For all of these samples the quenching effect saturated for light levels well below the maximum intensity of 10^{16} photons/cm^2 s. After turning the light off, the temperature was swept upward at rates from 0.05 to 0.4 K/s. This is the typical procedure used for thermally stimulated current measurements, in which the various traps are filled by the light-generated electrons and holes, and then the traps emit their carriers during the temperature sweep and produce current peaks at temperatures corresponding to the trap energy levels. A few such traps were also present in these materials and so had to be "cleaned out" before studying the quenching behavior. The cleaning procedure consisted simply of heating the sample to about 120 K, below the quenching recovery temperature, and then cooling again to 82 K. In this way, the interfering traps were emptied and so did not affect the current in subsequent temperature sweeps. Note also in Fig. 1 that the I vs T^{-1} curves begin to flatten out at low temperatures. This is due to hopping conduction, as evidenced by a sharp drop of the Hall coefficient, but the hopping phenomenon will not be discussed further here. It is also important to point out that below 120 K the quenched system is in equilibrium; i.e., the curves in Fig. 1 are reproduced no matter in which direction temperature is swept. The same is true, of course, above about 140 K, at which point all of the metastable defects have recovered to their ground states.

We will next model the quenching and recovery processes according to Eqs. (1) and (2). Let the total 0.15-eV donor density N_D consist of unquenched (ground state) donors, of density N_{D1} and transition energy E_{D1}, and quenched (metastable state) donors of density N_{D2} and transition energy E_{D2}. (Other possibilities will be discussed later.) Although we might normally assume that E_{D1} and E_{D2} would refer to $(0/+)$ transitions, there is evidence that they may refer to $(+/++)$ transitions instead. That is, a Brooks-Herring analysis of mobility μ vs temperature T suggests that $N_A \simeq 1.3\times10^{16}$ cm^{-3}, whereas $N_A^{\text{net}} \simeq 4\times10^{15}$ cm^{-3} from the n vs T analysis. For the $(0/+)$ transition, $N_A^{\text{net}} = N_A - N_{DS}$, while for the $(+/++)$ transition $N_A^{\text{net}} = N_A - N_{DS} - N_D$, where N_{DS} is the concentration of shallow donors (i.e., donors with energies well above E_F). Either of these equations for N_A^{net} is consistent with the calculated values of N_D, N_A, and N_A^{net}; in particular, the $(+/++)$ equation, if relevant, would suggest that N_{DS} is negligible since then $N_A^{\text{net}} = N_A - N_D$.

Since the highest value of n in the transition region is about 10^{12} cm^{-3}, we can set $n \ll N_A^{\text{net}}$ in Eq. (1). Then the solution for n is

$$n = \frac{1}{2}\left[\frac{N_D - N_{D2}}{N_A^{\text{net}}} - 1\right]\phi_1 + \frac{1}{2}\left[\frac{N_{D2}}{N_A^{\text{net}}} - 1\right]\phi_2 + \left\{\left[\frac{1}{2}\left[\frac{N_D - N_{D2}}{N_A^{\text{net}}} - 1\right]\phi_1 + \frac{1}{2}\left[\frac{N_{D2}}{N_A^{\text{net}}} - 1\right]\phi_2\right]^2 + \left[\frac{N_D}{N_A^{\text{net}}} - 1\right]\phi_1\phi_2\right\}^{1/2} . \tag{3}$$

Before quenching, $N_{D2} = 0$, so that

$$n_{unQ} = \left[\frac{N_D}{N_A^{\text{net}}} - 1\right]\phi_1 = \left[\frac{N_D}{N_A^{\text{net}}} - 1\right]\frac{g_u}{g_o} N_C' e^{\alpha/k} T^{3/2} e^{-E_{D1}/kT} . \tag{4}$$

After quenching, say at $T \leq 110$ K, n drops by more than three orders of magnitude, which could only be true if $(N_D - N_{D2})/N_A^{\text{net}} \simeq 1$ and $\phi_2 \ll \phi_1$, according to Eq. (1). Thus, in the quenched state, $N_{D2} = N_D - N_A^{\text{net}}$, and $E_{D2} > E_{D1}$, which means that the *occupied* donors [i.e., the (0) donors if the transition is $(0/+)$ or the $(+)$ donors if the transition is $(+/++)$] are the ones that quench, and they must attain a lower transition energy. Note that this is also the case with $EL2$ [the (0) states, or occupied states in the $(0/+)$ transition, quench and evidently push the metastable $(0/+)$ transition close to the edge of the valence band,[4,5] although this transition has never been directly observed]. Thus in the quenched state we will have

$$n_Q = \left[\left[\frac{N_D}{N_A^{\text{net}}} - 1\right]\phi_1\phi_2\right]^{1/2} = \left[\frac{N_D}{N_A^{\text{net}}} - 1\right]^{1/2} \frac{g_u}{g_o} N_C' e^{\alpha/k} T^{3/2} e^{-(E_{D1}+E_{D2})/2kT} , \tag{5}$$

where we have assumed that g_u/g_o and α are the same for the quenched and unquenched transitions. Note that Eqs. (4) and (5) give us an immediate test of the model, namely that

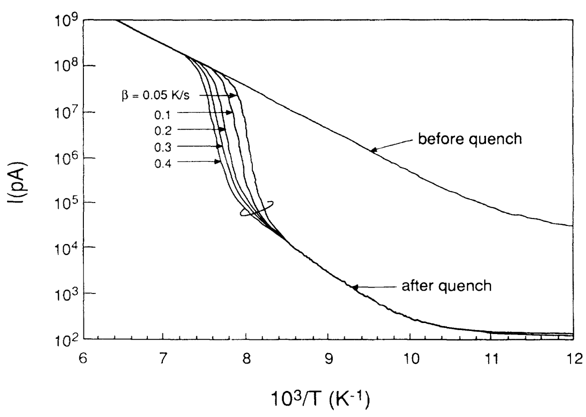

FIG. 1. Current vs inverse temperature for sample CS 3417 before and after an IR quench. The quantity β designates the heating rate.

$$\frac{n_{unQ}}{n_Q}=\left[\frac{N_D}{N_A^{\rm net}}-1\right]^{1/2}e^{(E_{D2}-E_{D1})/2kT}. \quad (6)$$

The unquenched data [Eq. (4)] give $E_1=0.155$ eV, and the values of n_{unQ} and n_Q, say at 110 K, would predict from Eq. (6) that $E_2=0.292$ eV. Then, the slope of the quenched data below the recovery temperature should be, according to Eq. (5), $(E_{D1}+E_{D2})/2=0.224$ eV, very close to what is observed. This is a strong indication that our model is basically correct, and that the metastable-state transition energy [(+/++) or (0/+)] drops about 0.14 eV relative to the ground-state transition energy. Also, note that we are directly observing the metastable state.

The analysis presented so far began with the assumption that N_{D2} represents the quenched donor and indeed, one unique consequence of that analysis, the relationship given by Eq. (6), agrees well with the data. However, another possibility which must be considered is that N_{D2} is a totally independent donor (having a transition energy $E_{D2}=0.224$ eV) which is simply "exposed" by the quench due to (1) acceptors being created by the quench and totally compensating N_{D1}, or (2) all of the N_{D1} donors being transformed to a deep donor metastable state which lies well below E_{D2} (like the $EL2$ case). The first idea, that acceptors are created by the quench, is inconsistent with our mobility results, namely that mobility is nearly unchanged by the quench. The second idea, that the metastable state is very deep and therefore out of the picture, would still require that the independent 0.224-eV center, which is "exposed" by the quench, have just the correct concentration, degeneracy, and temperature coefficient to give the observed value of n_{unQ}/n_Q [cf. Eq. (6)]. Furthermore, this scenario would require that the 0.224-eV center not itself quench, or E_F would drop even lower. We have observed centers at 0.127, 0.152, 0.160, 0.169, and 0.199 eV in various "0.15-eV" samples, and they all quench. These facts thus support our original hypothesis, namely that N_{D2} represents the quenched state of the 0.15-eV donor, and is not an independent donor.

We now consider the recovery of the quenched (metastable) states to their normal configurations. At the initial temperature T_i (82 K in our case) we have $N_{D2}=N_D-N_A^{\rm net}$, as noted before. An Auger-like recovery rate is usually written as $dN_{D2}/dt=-N_{D2}\sigma_n n v_n \exp(-E_b/kT)$, where σ_n is a cross section, $v_n=(2kT/m^*)^{1/2}$ is the thermal velocity, and E_b is a barrier energy. Attempts to use a pure thermal recovery mechanism (i.e., without the "nv_n" factor) give a very poor fit to the data. Thus, integrating the Auger-like rate with respect to time, and making a change of variable $T=T_i+\beta t$, the concentration of metastable centers is given by

$$N_{D2}(T)=(N_D-N_A^{\rm net})\exp\left\{-\int_{T_i}^{T}\frac{\sigma_n n v_n}{\beta}e^{-E_b/kT}dT\right\}. \quad (7)$$

Equations (2), (3), and (7) form an integral equation system, implicit in n. These equations were fitted to the n vs T data for $\beta=0.4$ K/s, and an excellent fit was achieved, as shown in Fig. 2. The *same* fitting parameters also reproduced the $\beta=0.05$ K/s data very well, as seen in the same figure. [Note that the data in Fig. 2 were derived from the I data in Fig. 1 by first correcting the I data for the temperature dependence of mobility ($I=C\mu n$) and then normalizing the unquenched data at one point to obtain C. As stated earlier, Hall-effect measurements show that mobility changes very little as a function of quenching.] The fit to the curves of Fig. 2 gives $\sigma_n=2\times10^{-12}$ cm^2, and $E_b=0.18$ eV, values which can be compared with those found for $EL2$ ($\sigma_n=2\times10^{-14}$ cm^{-2} and $E_b=0.11$ eV).[1] It may be significant that the Auger rates for $EL2$ and the 0.15-eV center are within an order of magnitude of each other over the entire transition range 120–140 K.

We next discuss the nature of the defect. Because the ground-state transition energy of 0.15 eV is close to that of the most dominant defect produced by 1-MeV electron irradiation $E2$, known to be the As vacancy (or possibly a vacancy-interstitial Frenkel pair),[12] it is of interest to know if $E2$ will quench. Thus we irradiated a pure ($n\simeq1.5\times10^{15}$ cm^{-3}), 15-μm-thick, molecular-beam epitaxial GaAs layer until the 0.15-eV defect was dominant, as determined by the slope of the ln$I$ vs T^{-1} curve. This defect ($E2$) would not quench; therefore our present defect is not a simple As vacancy. However, there are also similarities to As_{Ga}, both in the metastability recovery rate, as mentioned above, and in the quenching spectrum, which peaks at $h\nu\simeq1.1$ eV. Thus a much better candidate would seem to be a combination of V_{As} and As_{Ga}, such as the nearest-neighbor As_{Ga}-V_{As} center which has been studied theoretically by Baraff and Schluter (BS).[13] BS find that this defect has three transitions within the band gap: (0/+), (+/++), and (++/+++), all of them associated with V_{As}-like (not As_{Ga}-like) wave functions. They also find that the (+) state has a metastable configuration, with the As atom moving to a position

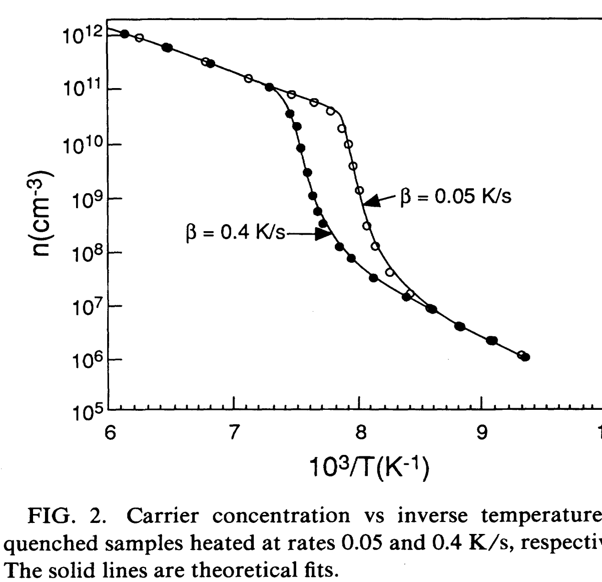

FIG. 2. Carrier concentration vs inverse temperature for quenched samples heated at rates 0.05 and 0.4 K/s, respectively. The solid lines are theoretical fits.

about 35% of the distance between the original As_{Ga} and V_{As} positions. [Interestingly enough, it appears from BS's Fig. 1 that the $(++)$ and $(+++)$ states may also have metastable configurations.] Finally, they show that IR illumination could induce this metastability by promoting an electron to an excited $(+)$ state which has a finite vibrational overlap with the metastable configuration of the ground $(+)$ state. Their calculations give an effective-mass-like ground-state $(0/+)$ transition close to the conduction band (CB), and a $(+/++)$ transition about 0.6 eV below the CB; our 0.15-eV result falls in between these values. However, perhaps more importantly, they find that the metastable-state $(+/++)$ transition falls about 0.2–0.3 eV below the ground-state $(+/++)$ transition, certainly within error of our value of 0.14 eV. BS state that "in so far as the Fermi energy is tied to these donor levels" (certainly true in our case) "it will drop during the ground state to metastable transition," which is exactly what we find. Elsewhere,[16] from binding- and formation-energy calculations, they argue that "nearest-neighbor As_{Ga}-V_{As} pairs should be an abundant defect in GaAs." Indeed, the only deep donors of high enough concentration to control E_F in bulk GaAs are this one at $E_C-0.15$ eV, another at $E_C-0.43$ eV (unknown), and $EL2$ at $E_C-0.75$ eV. All of our 0.15-eV samples also contain $EL2$, as determined by DLTS. For example, sample CS 3417, discussed here, was found to have $[EL2]=2\times10^{15}$ cm^{-3}. Thus As_{Ga} centers are available to form the As_{Ga}-V_{As} complexes.

Finally, as stated earlier, the metastable-to-ground-state recovery rate for our defect is similar to that of $EL2$ (or As_{Ga}). It is perhaps not unexpected that the recovery rate for As_{Ga}-V_{As} should be close to that for As_{Ga} alone, because the metastable states are basically V_{Ga}-As_i-V_{As} and V_{Ga}-As_i for ground states As_{Ga}-V_{As} and As_{Ga}, respectively, and the V_{Ga}-As_i distances are similar.[4,13] Thus, although the electronic states are quite different, the metastability barriers could be similar. However, a problem with the assignment of As_{Ga}-V_{As} as our center is the additional *bistability* of As_{Ga}-V_{As}, which in n-type material should result in a full jump of the As atom to the V_{As} site, leaving only V_{Ga}, which is an acceptor. Perhaps a next-nearest-neighbor pair of As_{Ga} and V_{As}, or a complex involving a third component, would be better candidates.

In summary, we have observed a metastable state of the well-known $E_C-0.15$-eV defect in GaAs, and determined its transition energy to be $E_C-0.29$ eV. Many of the properties of this defect are similar to those of the As_{Ga}-V_{As} center, elucidated theoretically by Baraff and Schluter, and predicted to be abundant in GaAs. However, we cannot rule out other possibilities even though we believe As_{Ga} and V_{As} are likely involved.

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